lution and washed with water. The white crystalline solid was crystallized from aqueous alcohol to provide **13a** (8.0 g, 93%) as a white powder: mp 308–310 °C; IR (KBr) 3200, 1625, 1600, 1390, 1200 cm^{-1}; NMR (CF_3COOD) δ 2.23 (m, 2 H), 2.70 (s, 3 H), 3.06 (m, 4 H), 6.97 (s, 1 H); CI mass spectrum (NH_3), *m/e* (relative intensity) 193 ($M^+ + 1$, 100).

Anal. Calcd for $C_{10}H_{12}N_2O_2$: C, 62.48; H, 6.29; N, 14.57. Found: C, 62.60; H, 6.52; N, 14.38.

4-Methyl-5,6,7,8-tetrahydro-5-(hydroxyimino)-2-hydroxyquinoline-5-acetate (13b). The oxime **13a** (0.50 g, 0.003 mol) obtained from the previous experiment was dissolved in a mixture of acetic acid (4 mL) and acetic anhydride (1.5 mL). The solution was saturated with anhydrous hydrogen chloride and then heated to reflux for 1 h. The light brown solution which resulted was cooled and diluted with water, and a white solid precipitated from the mixture. The material was crystallized from alcohol to provide **13b**: 0.43 g (70%); mp 268–270 °C; IR (KBr) 3450, 1760, 1650, 1610, 1580 cm^{-1}; NMR (warm Me_2SO) δ 1.63 (q, 2 H), 2.20 (s, 3 H), 2.40 (s, 3 H), 2.60 (m, 4 H), 6.10 (s, 1 H); CI mass spectrum (NH_3), *m/e* (relative intensity) 236 (18), 235 ($M^+ + 1$, 100), 177 (15).

Anal. Calcd for $C_{12}H_{14}N_2O_3$: C, 61.54; H, 5.98; N, 11.96. Found: C, 62.29; H, 5.95; N, 12.02.

4-Methyl-5-acetamido-2-quinolone (10). The oxime (**13a**; 0.5 g, 0.003 mol) was dissolved in a mixture of acetic acid (4 mL) and acetic anhydride (1.5 mL). The solution was saturated with anhydrous hydrogen chloride gas and then held at reflux for 18 h. At the end of the reaction period, the solution had become dark whereupon it was cooled, diluted with water, and allowed to stand for several hours. The white precipitate which formed was washed with water and crystallized from alcohol to provide the quinolone **10**: 0.30 g (53%); mp 355 °C; IR (KBr) 3280, 1690, 1650, 1610, 1535 cm^{-1}; NMR (warm Me_2SO, 220 MHz) δ 2.04 (s, 3 H), 2.41 (2 s, 3 H, rotomers), 6.32 (s, 1 H), 6.93 (d, 1 H), 7.25 (d, 1 H), 7.43 (t, 1 H), 9.72 (s, 1 H); CI mass spectrum (NH_3), *m/e* (relative intensity) 218 (16), 217 ($M^+ + 1$, 100), 216 (14).

Anal. Calcd for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.50; N, 12.96. Found: C, 66.41; H, 5.28; N, 13.05.

There were two other materials (20%) present in the mother liquor of this reaction mixture. One of these compounds still contained a signal due to methylene protons; however, it was present in only minute quantities, and it was not possible to separate the compound from the starting material (**13a** or **13b**).

2,5-Dihydroxy-1,6-diazaphenalene-1-acetamide (15b). The *N*-oxide **14** (2.0 g, 0.009 mol) was dissolved in acetic acid (32 mL) and acetic anhydride (12 mL), after which the solution was saturated with hydrogen chloride gas. The mixture was heated to reflux for 18 h, cooled, and diluted with water, and the precipitate which formed upon standing was filtered from the medium. The green solid was washed with water, dissolved in acetic acid, and reprecipitated upon dilution with water. The orange-green solid obtained from this treatment was dried to provide **15b**: 1.7 g (86%); mp >350 °C; IR (KBr) 3200, 1670, 1630, 1600, 1370, 1300 cm^{-1}; NMR (warm Me_2SO, 60 MHz) δ 2.50 (s, 3 H), 6.20 (s, 1 H), 6.60–7.30 (m, 4 or 5 H), 10.57 (s, 1 H), 11.60 (s, 1 H) (on addition of D_2O, the singlets at δ 10.57 and 11.60 disappeared); NMR (CF_3COOH) δ 2.80 (s, 3 H), 7.00–8.00 (m, 5 H); CI mass spectrum (NH_3), *m/e* (relative intensity) 244 (19), 243 ($M^+ + 1$, 100), 242 (17), 201 (13).

Anal. Calcd for $C_{13}H_8N_2O_2$: C, 64.46; H, 4.13; N, 11.57. Found: C, 64.43; H, 3.97; N, 11.48.

N.B. When the reaction was scaled up to the 8-g level, the yield fell off considerably, and **15b** was contaminated with other material. It was felt that some dimeric material may be the contaminant; however, numerous attempts to observe a dimer (CI mass spectroscopy) failed; moreover, the product contained no methylene protons, and therefore any dimer formation (if present) would have occurred after the Semmler–Wolff aromatization took place.

Registry No. **10**, 73636-01-8; **11**, 61062-45-1; **12**, 29707-35-5; **13a**, 73636-02-9; **13b**, 73636-03-0; **14**, 68871-44-3; **15b**, 73636-04-1.

Studies on Ketene and Its Derivatives. 100.[1] 1-(Dimethylphosphono)- and 1-(Diphenylphosphinyl)-5-oxo-4-oxaspiro[2.3]hexanes. Synthesis and Some Reactions

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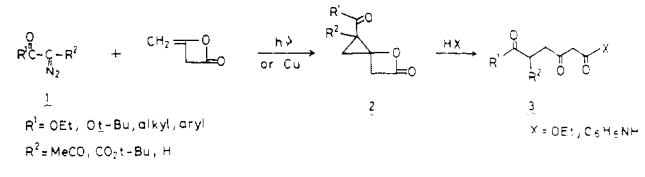
Reaction of diketene with dimethyl (α-diazoalkyl)phosphonates **4–8** and (diazomethyl)diphenylphosphine oxide (**14**) under irradiation gave *E* and *Z* 1-substituted 1-(dimethylphosphono)-5-oxo-4-oxaspiro[2.3]hexanes **9a,b–13a,b** and (*E*)- and (*Z*)-1-(diphenylphosphinyl)-5-oxo-4-oxaspiro[2.3]hexanes (**15a,b**), respectively. The stereochemical assignment was made on the basis of the NMR spectral data. Methanolysis of 1-(dimethylphosphono)-5-oxo-4-oxaspiro[2.3]hexane (**9**) and 1-(dimethylphosphono)-1-phenyl-5-oxo-4-oxaspiro[2.3]hexane (**11**) gave dimethyl 4-(methoxycarbonyl)-3-oxobutylphosphonates **16** and **17**. Treatment of **9** and **11** with anilines gave dimethyl 4-(*N*-arylcarbamoyl)-3-oxobutylphosphonates **18a–d** and **19a–d**. Compounds **9** and **11** reacted with *o*-phenylenediamine and phenols to give 4-[2-(dimethylphosphono)ethyl]-1,5-benzodiazepin-2-ones **20** and **21** and 4-[2-(dimethylphosphono)ethyl]-7-hydroxycoumarin derivatives **22a,b** and **23a,b**, respectively. Compound **11** and (*E*)-1-(dimethylphosphono)-1-(*p*-methoxyphenyl)-5-oxo-4-oxaspiro[2.3]hexane (**12a**), on treatment with methyl acetoacetate in the presence of sodium hydride, underwent ring transformation to give 2-cyclopentenones **24** and **25**.

Previously, we have reported reactions of diketene with α-diazo ketones and esters **1**, in the presence of copper powder or under irradiation, to give 1-substituted 5-oxo-4-oxaspiro[2.3]hexanes **2**[2–4] (Scheme I). Compounds of type **2**, upon treatment with nucleophiles, undergo opening

Scheme I

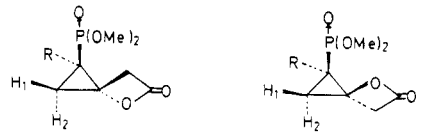


of β-lactone and cyclopropane rings to give β-keto carboxylic acids **3**, which subsequently cyclize to heterocycles.[3,4] The reactions which form **2** are taken to involve

(1) Part 99: Kato, T.; Chiba, T.; Sasaki, T., *Yakugaku Zasshi*, **1980**, *100*, 571.
(2) Kato, T.; Katagiri, N. *Chem. Pharm. Bull.* **1973**, *21*, 729.
(3) Kato, T.; Katagiri, N.; Sato, R. *J. Chem. Soc., Perkin Trans 1* **1979**, 525.
(4) Kato, T.; Katagiri, N.; Sato, R. *Chem. Pharm. Bull.* **1979**, *27*, 1176.

0022-3263/80/1945-2587$01.00/0

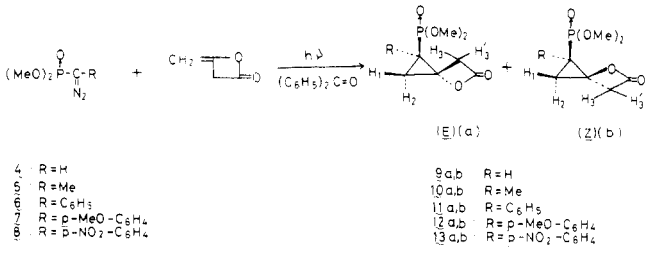
Table I. Chemical Shifts and Coupling Constants of Cyclopropane Ring Protons of (*E*)- and (*Z*)-1-(Dimethylphosphono)-5-oxo-4-oxaspiro[2.3]hexanes 10a,b-13a,b[a]



compd	R	H_1 δ	H_1 J_{H_1P}	H_1 $J_{H_1H_2}$	H_2 δ	H_2 J_{H_2P}	H_1 δ	H_1 J_{H_1P}	H_1 $J_{H_1H_2}$	H_2 δ	H_2 J_{H_2P}
10	Me	1.65	18.5	7.2	1.27	13.0	2.04	20.1	7.2	1.08	12.0
11	C_6H_5	2.13	18.2	7.2	1.90	13.0	2.48	20.4	7.4	1.76	11.5
12	*p*-MeO-C_6H_4	2.05	18.1	7.0	1.83	13.0	2.40	20.0	7.2	1.75	11.5[b]
13	*p*-NO_2-C_6H_4	2.22	19.0	7.8	1.95	12.8	2.59	19.2	8.0	1.83	11.4

[a] Spectra were obtained in $CDCl_3$, chemical shifts are in δ relative to tetramethylsilane, and the coupling constants are given in hertz. [b] The spectrum showed a mixture of **12a** and **12b**.

Scheme II



the addition of carbenes to the exo double bond of diketene. In contrast to familiar reactions of diketene, which proceed heterolytically to give ring-opened products, there are few examples concerning the reactions which give products bearing the β-lactone moiety intact.[5]

In the present paper we report continuation of our investigation of the synthesis of 5-oxo-4-oxaspiro[2.3]hexanes and their reactions with various nucleophiles, some of which involve novel ring transformation to cyclopentenones.

Results and Discussion

Synthesis of 1-(Dimethylphosphono)- and 1-(Diphenylphosphinyl)-5-oxo-4-oxaspiro[2.3]hexanes. When dimethyl (diazomethyl)phosphonate (**4**) was allowed to react with diketene under irradiation in the presence of benzophenone in dichloromethane, (*E*)-1-(dimethylphosphono)-5-oxo-4-oxaspiro[2.3]hexane (**9a**) [bp 70–72 °C (0.002 mm)] and its *Z* isomer **9b** [bp 95–97 °C (0.005 mm)] were obtained in 48 and 39% yields, respectively (Scheme II).

The structures of **9a** and **9b** were determined on the basis of elemental analyses and spectral data. The IR spectra of both compounds **9a** and **9b** showed β-lactone carbonyl absorption at 1850 cm^{-1} but no absorption characteristic of a C=C bond. Therefore, both compounds **9a** and **9b** are judged to be stereoisomeric 5-oxo-4-oxaspiro[2.3]hexane derivatives, formed by the addition of carbene to the exo double bond of diketene.

The configurations of compounds **9a** and **9b** are shown by comparison of their NMR spectra with those of analogous compounds obtained before.[2-4] Specifically, in the NMR spectrum of compound **9a** a signal due to the methylene protons of the β-lactone ring is observed at δ 3.61–4.05 as an AB quartet, further split into a multiplet by coupling with the phosphorus atom, whereas that of compound **9b** is observed at δ 3.78 as a singlet. Inasmuch as the β-lactone methylene protons of **9a** are *Z* to the dimethylphosphono group, and thus proximal, whereas those of **9b** are *E* and more distant, the isomer with the greater splitting by phosphorus is identified as **9a**. The NMR signals due to the cyclopropane ring protons are difficult to assign because of the complexity of the spectrum. The NMR spectrum of compound **9a** shows a multiplet due to the cyclopropane ring protons at δ 1.38–1.84 whereas that of compound **9b** presents a multiplet at δ 1.42–2.20. It does appear, however, that the lower field signal of compound **9b** can be assigned to an H_1 proton of the cyclopropane ring because the H_1 proton should be shifted to lower field by the effect of the *Z* dimethylphosphono group and the *Z* ring oxygen of the β-lactone.[2-4]

These two observations based on the NMR spectra indicate compounds **9a** and **9b** to be (*E*)-1-(dimethylphosphono)-5-oxo-4-oxaspiro[2.3]hexane and its *Z* isomer, respectively.

Next, the reaction of diketene with dimethyl (α-diazoethyl)phosphonate (**5**) under similar conditions was carried out to give (*E*)-1-(dimethylphosphono)-1-methyl-5-oxo-4-oxaspiro[2.3]hexane [**10a**; bp 73–75 °C (0.002 mm)] and its *Z* isomer **10b** [bp 93–95 °C (0.002 mm)] in 39 and 38% yields, respectively. The configurations of compounds **10a** and **10b** were elucidated from the chemical shifts and coupling constants of cyclopropane ring protons (Table I). The chemical shifts of cyclopropane ring protons should be affected mainly by the β-lactone oxygen and the dimethylphosphono group. The lowest chemical shift at δ 2.04 is attributed to the signal due to an H_1 proton of the *Z* isomer **10b**. The *J* value of 20.1 Hz is consistent with the coupling constant between H_1 and the phosphorus atom of **10b**, whereas the δ value of 1.08 and the smaller coupling constant of 12.0 Hz (J_{H_2P}) are ascribed to the H_2 signal of the *Z* isomer **10b**.[6] At the same time, the signals at δ 1.65 and 1.27 are attributable to the H_1 and H_2 protons of the *E* isomer **10a**.

Similarly, the light-induced reaction of dimethyl-(diazoarylmethyl)phosphonates **6–8** with diketene afforded the (*E*)- and (*Z*)-5-oxo-4-oxaspiro[2.3]hexane derivatives **11a,b–13a,b**. In the case of the reaction of **7**, the *E* isomer **12a** was obtained as the main product. Although the *Z*

(5) Kato, T. *Acc. Chem. Res.* **1974**, *7*, 265.

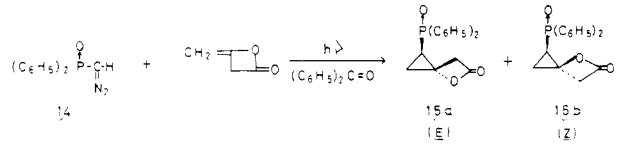
(6) It is well established that, in the vicinal coupling between proton and phosphorus atom, the *Z* coupling constant is larger than the *E* coupling constant. Scherer, H.; Hartmann, A.; Regitz, M.; Tunggal, B. D.; Günther, H. *Chem. Ber.* **1972**, *105*, 3357.

Table II. Reaction of Diketene with Dimethyl (α-Diazoalkyl)phosphonates 4-8[a]

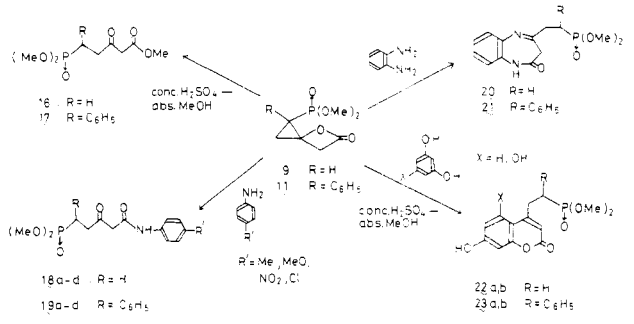
(α-diazoalkyl)phosphonate					
no.	R	amt, g (mmol)	product (amt, g)	yield, %	mp or bp (mm), °C
4	H	1.73 (12)	**9a** (1.13)	48	70-72 (0.002)
			9b (0.91)	39	95-97 (0.005)
5	Me	1.98 (12)	**10a** (1.04)	39	73-75 (0.002)
			10b (1.02)	38	93-95 (0.002)
6	C_6H_5	1.57 (7)	**11a** (0.66)	35	127[b]
			11b (0.78)	41	120-122[b]
7	*p*-MeO-C_6H_4	2.56 (10)	**12a** (2.30)	74	124[b]
			12b		
8	*p*-NO_2-C_6H_4	7.27 (27)	**13a** (2.03)	25	130[c]
			13b (2.27)	28	156-157[c]

[a] Satisfactory analytical values were reported for all compounds in Tables II, III, and IV. Spectral data of all compounds are provided as supplementary material. [b] Ether-chloroform as recrystallization solvent. [c] Benzene as recrystallization solvent.

Scheme III



Scheme IV



isomer **12b** was not isolated, the NMR spectrum of the product mixture showed its formation in low yield.

Chemical shifts and coupling constants of cyclopropane ring protons of **10a,b**–**13a,b** are summarized in Table I. In the cases of both the *E* and *Z* isomers, the coupling constant (18.1–20.4 Hz) between H_1 and the phosphorus atom is larger than that (11.4–13.0 Hz) between H_2 and the phosphorus atom. Of the four protons (*E* H_1, H_2 and *Z* H_1, H_2), H_1 of the *Z* isomer shows the lowest chemical shift while the signal of H_2 of the *Z* isomer is observed in the highest field. Results of these reactions are summarized in Table II.

Cyclopropanations of olefins by phosphorylcarbenes generated from dimethyl (α-diazoalkyl)phosphonates with copper catalysis have been reported.[6,7] However, the reaction of diketene under the same conditions gave a low yield of 5-oxo-4-oxaspiro[2.3]hexane derivatives.

Reaction of (diazomethyl)diphenylphosphine oxide (**14**) with diketene under the same conditions gave two products, to which we assign spiro structures, namely, (*E*)-1-(diphenylphosphinyl)-5-oxo-4-oxaspiro[2.3]hexane (**15a**) and its *Z* isomer **15b** (Scheme III). As detailed in the Experimental Section, the spectral data are consistent with those structures.

Reaction of 1-(Dimethylphosphono)-5-oxo-4-oxaspiro[2.3]hexanes 9a,b, 11a,b, and 12a. When spiro compound **9** (a mixture of **9a** and **9b**) was heated in absolute methanol in the presence of concentrated sulfuric acid, dimethyl [4-(methoxycarbonyl)-3-oxobutyl]-phosphonate (**16**) was obtained in 65% yield (Scheme IV). Similar treatment of compound **11** (a mixture of **11a** and **11b**) afforded dimethyl [4-(methoxycarbonyl)-3-oxo-1-phenylbutyl]phosphonate (**17**) in 97% yield.

Reactions of compound **9** with aniline derivatives such as *p*-toluidine, *p*-anisidine, *p*-nitroaniline, and *p*-chloroaniline gave the corresponding dimethyl (4-carbamoyl-3-oxobutyl)phosphonates **18a–d**. Similar reactions of compound **11** with anilines afforded the corresponding carbamoyl derivatives **19a–d**. The results are summarized in Table III.

Table III. Yields and Melting Points of Dimethyl [4-(*N*-Arylcarbamoyl)-3-oxobutyl]phosphonates 18a-d and 19a-d[a]

compd	R	R'	yield, %	mp, °C
18a	H	Me	80	85-86[b]
18b	H	OMe	70	97-98[b]
18c	H	NO_2	80	175[c]
18d	H	Cl	81	128-129[d]
19a	C_6H_5	Me	71	107-108[e]
19b	C_6H_5	OMe	68	119-120[e]
19c	C_6H_5	NO_2	61	179[f]
19d	C_6H_5	Cl	74	128-129[e]

[a] See the corresponding footnote in Table II. [b] Isopropyl ether-benzene as recrystallization solvent. [c] Benzene-chloroform as recrystallization solvent. [d] Benzene as recrystallization solvent. [e] Ether-benzene as recrystallization solvent. [f] Benzene-ethyl acetate as recrystallization solvent.

Similar reactions of *o*-phenylenediamine with the spiro compounds **9** and **11** afforded benzodiazepinones **20** and **21**, respectively.

Reactions of compound **9** with resorcinol and phloroglucinol gave coumarin derivatives **22a** and **22b**. Similarly, compound **11** was transformed into coumarin derivatives **23a** and **23b** in good yields. The results are summarized in Table IV.

Reaction of methyl acetoacetate with compound **11** in tetrahydrofuran (THF) in the presence of sodium hydride gave 4-(dimethylphosphono)-3-hydroxy-4-phenyl-2-cyclopenten-1-one (**24**) in 92% yield. It should be noted that **24** is an isomer of **11** and that the sodio derivative of methyl acetoacetate acts only as a catalyst in this reaction. The use of potassium *tert*-butoxide instead of methyl sodioacetoacetate gave a lower yield of compound **24**.

Similar reaction of compound **12a** with methyl acetoacetate gave 4-(dimethylphosphono)-3-hydroxy-4-(*p*-methoxyphenyl)-2-cyclopenten-1-one (**25**) in 79% yield (Scheme V).

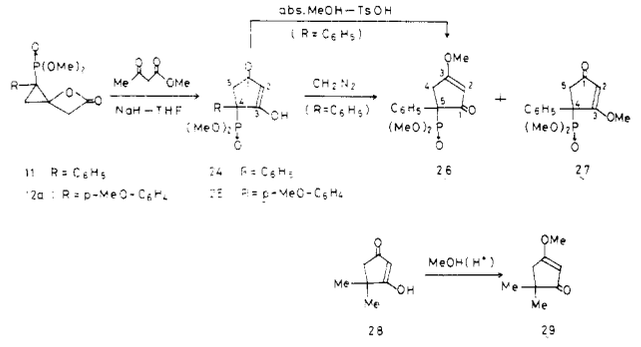
(7) (a) Seyferth, D.; Hilbert, P.; Marmor, R. S. *J. Am. Chem. Soc.* **1967**, *89*, 4811. (b) Seyferth, D.; Marmor, R. S. *Tetrahedron Lett.* **1970**, 2493. (c) Seyferth, D.; Marmor, R. S.; Hilbert, P. *J. Org. Chem.* **1971**, *36*, 1379.

Table IV. Reactions of 1-(Dimethylphosphono)-5-oxo-4-oxaspiro[2.3]hexanes 9 and 11 with Phenols[a]

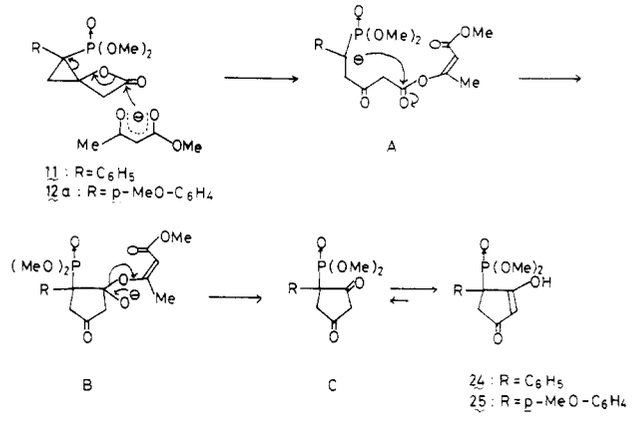
hexane no.	hexane amt, g (mmol)	phenol (amt, g, mmol)	product no.	R	X	yield, g (%)	mp, °C
9[b]	0.41 (2)	resorcinol (0.22, 2)	22a	H	H	0.39 (65)	185[c]
9	0.41 (2)	phloroglucinol (0.25, 2)	22b	H	OH	0.45 (68)	233-234[d]
11[b]	0.28 (1)	resorcinol (0.11, 1)	23a	C_6H_5	H	0.23 (62)	218-219[e]
11	0.56 (2)	phloroglucinol (0.25, 2)	23b	C_6H_5	OH	0.47 (58)	262-263[e]

[a] See the corresponding footnote in Table II. [b] A mixture of *E* and *Z* isomers. [c] Ethyl acetate as recrystallization solvent. [d] Ethanol-ethyl acetate as recrystallization solvent. [e] Ethanol as recrystallization solvent.

Scheme V



Scheme VI



Methylation of cyclopentenone derivative **24** with diazomethane gave 5-(dimethylphosphono)-3-methoxy-5-phenyl-2-cyclopenten-1-one (**26**) and 4-(dimethylphosphono)-3-methoxy-4-phenyl-2-cyclopenten-1-one (**27**) in 38 and 35% yields, respectively. Compound **26** was also obtained in 75% yield by methylation of compound **24** with absolute methanol in the presence of *p*-toluenesulfonic acid.

In the NMR spectra, a signal due to the methylene protons of compound **26** is observed at lower field (δ 2.95–3.85) than that for compound **27** (δ 2.58–3.70). A signal due to the olefinic proton (δ 5.97) of compound **26** appears as a triplet, owing to coupling with methylene protons, whereas the signal due to the olefinic proton of compound **27** is observed at δ 5.56 as a doublet (J = 2.0 Hz), owing to coupling with a phosphorus atom. These data are consistent with the 5-(dimethylphosphono)-2-cyclopenten-1-one (**26**) and the 4-(dimethylphosphono)-2-cyclopenten-1-one (**27**) structures.

Obviously, treatment of compound **24** with *p*-toluenesulfonic acid in absolute methanol resulted in rearrangement of the C=C double bond to give the 5-(dimethylphosphono)-2-cyclopenten-1-one derivative **26**. Such a shift of the double bond finds analogy in the reported formation of 3-methoxy-5,5-dimethyl-2-cyclopenten-1-one (**29**) by the methylation of 3-hydroxy-4,4-dimethyl-2-cyclopenten-1-one (**28**) with methanol in the presence of acid as a catalyst.[8]

Formation of the cyclopentenones **24** and **25** from spiro compounds **11** and **12a** can be explained as follows. Nucleophilic attack of an acetoacetate carbanion on the carbonyl carbon of spiro compound **11** or **12a** causes ring fission to form the β-(acyloxy)crotonate derivative A as an intermediate (Scheme VI). Cyclization of intermediate A gives the cyclopentanone B, from which methyl acetoacetate eliminates as an anion to give the cyclopentanedione C, which exists in the enol forms **24** and **25**.

(8) Landesberg, J. M.; Kellner, D. *J. Org. Chem.* **1968**, *33*, 3374.

Experimental Section

IR spectra were taken with a JASCO IR-S spectrophotometer and data are reported in reciprocal centimeters. NMR spectra were recorded by using tetramethylsilane as an internal standard on Hitachi Model R-20A and JEOL Model PS-100 spectrometers at 60 and 100 MHz, respectively. Melting and boiling points are uncorrected. The ultraviolet (UV) light source was a Riko UVL-100HA, water-cooled, high-pressure, mercury lamp (Pyrex filter).

General Procedure for the Synthesis of 1-(Dimethylphosphono)-5-oxo-4-oxaspiro[2.3]hexane Derivatives 9a,b–13a,b. A solution of 7–27 mmol of dimethyl (α-diazoalkyl)phosphonate (**4–8**),[9] 1 molar equiv of benzophenone, and ca. 10 molar equiv of diketene in 50 mL of CH_2Cl_2 was irradiated with a mercury lamp (100 W) under a nitrogen atmosphere with ice cooling for 2 h. Excess diketene and CH_2Cl_2 were evaporated under reduced pressure below 50 °C. The resulting residue was washed three times with 30 mL of hexane–benzene (20:1) to remove benzophenone. An insoluble part was subjected to silica gel (20–50 g) column chromatography. Elution with hexane gave benzophenone. The column was developed successively with 1 L each of a mixture of hexane and chloroform (20:1, 10:1, 5:1, 3:1, and 1:1), and elution was continued with chloroform or chloroform–ethyl acetate to give (*E*)- and (*Z*)-1-(dimethylphosphono)-5-oxo-4-oxaspiro[2.3]hexanes **9a,b–13a,b**. Column chromatography followed by fractional recrystallization from ether gave compounds **11a** and **11b**. The results are summarized in Table II.

(*E*)- and (*Z*)- 1-(Diphenylphosphinyl)-5-oxo-4-oxaspiro[2.3]hexanes (15a and 15b). A solution of 1.16 g (5 mmol) of (diazomethyl)diphenylphosphine oxide (**14**),[9] 4.2 g (50 mmol) of diketene, and 0.87 g (5 mmol) of benzophenone in 50 mL of CH_2Cl_2 was irradiated with a high-pressure mercury lamp (100 W) under a nitrogen atmosphere with ice cooling for 2 h. Excess diketene and CH_2Cl_2 were removed under reduced pressure below 50 °C.

(9) For the preparation of dimethyl (α-diazoalkyl)phosphonates and (diazomethyl)diphenylphosphine oxide, see: Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 222, and references therein.

The residue was washed with 20 mL of ether–hexane (1:3) to remove benzophenone. The resulting residue was extracted with 30 mL of ether. The ethereal extract was condensed to give a crystalline substance, which was recrystallized from ether–chloroform to afford 0.17 g of **15a** as colorless needles.

The ether-insoluble part was extracted with 30 mL of chloroform. The chloroform solution was condensed to 10 mL and kept at −20 °C overnight to give a crystalline substance, which was purified by recrystallization from chloroform to afford 0.16 g of **15b** as colorless needles. The chloroform-insoluble part was subjected to silica gel (10 g) column chromatography. After elutriation with 4 L of hexane–chloroform (1:1), the column was developed with chloroform to give 0.32 g of **15a**. Subsequent elution with ethyl acetate gave 0.29 g of **15a**. Total yields of **15a** and **15b** were 0.49 g (34%) and 0.45 g (32%), respectively.

15a: mp 150 °C; IR ($CHCl_3$) 1845 (C=O), 1270 (P=O) cm^{-1}, NMR ($CDCl_3$) δ 1.70–2.36 (m, 3 H, cyclopropane ring protons), 3.68–4.04 (AB q, 2 H, J = 18.0 Hz, β-lactone ring protons), 7.40–8.08 (m, 10 H, aromatic protons). Anal. Calcd for $C_{17}H_{15}O_3P$: C, 68.41; H, 5.03. Found: C, 68.25; H, 5.07.

15b: mp 220–221 °C dec; IR ($CHCl_3$) 1850 (C=O), 1250 (P=O) cm^{-1}; NMR ($CDCl_3$) δ 1.47–2.36 (m, 3 H, cyclopropane ring protons), 3.78 (s, 2 H, β-lactone ring protons), 7.40–8.00 (m, 10 H, aromatic protons). Anal. Calcd for $C_{17}H_{15}O_3P$: C, 68.41; 5.03. Found: C, 68.41; H, 5.07.

Dimethyl [4-(Methoxycarbonyl)-3-oxobutyl]phosphonate (16). A solution of 1.2 g (5.8 mmol) of **9**[10] and a catalytic amount of concentrated sulfuric acid in 10 mL of absolute methanol was warmed at 50 °C for 7 h. Evaporation of methanol left an oily residue, to which 10 mL of water was added. The mixture was extracted with chloroform. The chloroform extract was dried over anhydrous magnesium sulfate. Evaporation of the solvent gave an oil (1 g), which was subjected to column chromatography on silica gel (18 g). The column was developed with 0.5 L of hexane–chloroform (5:1) and successively with 0.5 L of hexane–chloroform (1:1). Elution with chloroform gave an oil, which was distilled under reduced pressure to give 0.9 g (65%) of **16**: bp 90–92 °C (0.003 mm); IR ($CHCl_3$) 1750 (CO_2Me), 1725 (C=O), 1245 (P=O), 1065 (POC) cm^{-1}; NMR ($CDCl_3$) δ 1.77–2.31 (m, 2 H), 2.66–3.15 (m, 2 H), 3.51 (s, 2 H), 3.72 (2 d, 6 H, J = 11.0 Hz, 2 $POCH_3$), 3.74 (s, 3 H, $COOCH_3$). Anal. Calcd for $C_8H_{15}O_6P \cdot {}^1/_4H_2O$: C, 39.59; H, 6.39. Found: C, 39.74; H, 6.56.

Dimethyl [4-(Methoxycarbonyl)-3-oxo-1-phenylbutyl]-phosphonate (17). A solution of 0.56 g (2 mmol) of **11**[10] and a catalytic amount of concentrated sulfuric acid in 5 mL of absolute methanol was warmed at 50 °C for 5 h. Workup as above gave 0.58 g (97%) of **17**: bp 107–110 °C (0.001 mm); IR ($CHCl_3$) 1750 (CO_2Me), 1730 (C=O), 1250 (P=O), 1065, 1040 (POC) cm^{-1}; NMR ($CDCl_3$) δ 3.10–4.10 (m, 14 H), 7.30 (s, 5 H, aromatic protons). Anal. Calcd for $C_{14}H_{19}O_6P$: C, 53.50; H, 6.05. Found: C, 53.59; H, 6.34.

General Procedure for the Synthesis of Dimethyl [4-(*N*-Arylcarbamoyl)-3-oxobutyl]phosphonates 18a–d and 19a–d. A mixture of 0.41 g (2 mmol) of **9** [or 0.56 g (2 mmol) of **11**] and 2 mmol of the aniline derivative was heated without solvent at 90 °C. The crystals obtained were purified by recrystallization from the appropriate solvent shown in Table III to give compounds **18a–d** and **19a–d**. When the crystalline substance was hard to separate, the reaction mixture was subjected to column chromatography on silica gel (5 g). The column was developed with 0.5 L of chloroform and then with ethyl acetate. Elution with ethyl acetate gave compounds **18a–d** and **19a–d**. The results are summarized in Table III.

4-[2-(Dimethylphosphono)ethyl]-1,5-benzodiazepin-2-one (20). A solution of 0.41 g (2 mmol) of **9** and 0.23 g (2 mmol) of *o*-phenylenediamine in 5 mL of absolute methanol was heated at 50 °C for 9 h. Evaporation of methanol left an oily residue, which was kept overnight at room temperature to give a crystalline substance. Purification by recrystallization from benzene gave 0.45 g (76%) of **20** as colorless needles: mp 108–109 °C; IR ($CHCl_3$) 3400 (NH), 1680 (C=O), 1645 (C=N), 1245 (P=O), 1070, 1045 (POC) cm^{-1}; NMR ($CDCl_3$) δ 1.98–3.15 (m, 4 H), 3.13 (s, 2 H, 3-CH_2), 3.75 (2 d, 6 H, J = 10.8 Hz, 2 $POCH_3$), 7.05–7.35 (m, 4 H, aromatic protons), 9.13 (br s, 1 H, NH). Anal. Calcd for $C_{13}H_{17}N_2O_4P \cdot {}^1/_4H_2O$: C, 51.82; H, 5.81; N, 9.30. Found: C, 52.02; H, 5.64; N, 9.31.

4-[2-(Dimethylphosphono)-2-phenylethyl]-1,5-benzodiazepin-2-one (21). A solution of 0.56 g (2 mmol) of **11** and 0.56 g (2 mmol) of *o*-phenylenediamine in 5 mL of absolute methanol was heated at 50 °C for 25 h. Evaporation of methanol gave a crystalline substance, which was recrystallized from benzene to afford 0.53 g (67%) of **21** as colorless needles: mp 159–160 °C; IR ($CHCl_3$) 3420 (NH), 1685 (C=O), 1645 (C=N), 1245 (P=O), 1065, 1035 (POC) cm^{-1}; NMR (Me_2SO-d_6) δ 3.02 (s, 2 H, 3-CH_2), 3.10–3.92 (m, 3 H), 3.44 (d, 3 H, J = 10.7 Hz, $POCH_3$), 3.60 (d, 3 H, J = 10.7 Hz, $POCH_3$), 7.10–7.60 (m, 4 H, aromatic protons), 7.12 (s, 5 H, aromatic protons), 10.26 (br s, 1 H, NH). Anal. Calcd for $C_{19}H_{21}N_2O_4P$: C, 61.29; H, 5.65; N, 7.53. Found: C, 61.63; H, 5.65; N, 7.51.

General Procedure for the Synthesis of 4-[2-(Dimethylphosphono)ethyl]-7-hydroxycoumarin Derivatives 22a,b and 23a,b. A solution of **9** (or **11**), the phenol derivative, and a catalytic amount of concentrated sulfuric acid in 5 mL of absolute methanol was heated at 50 °C for 8 h. Evaporation of methanol gave a crystalline residue, to which 5 mL of water was added. The mixture was extracted with chloroform. The chloroform solution was dried over anhydrous magnesium sulfate. Evaporation of chloroform gave a crystalline substance, which was recrystallized from the appropriate solvent shown in Table IV to afford coumarin derivatives **22a,b** and **23a,b**. The results are summarized in Table IV.

4-(Dimethylphosphono)-3-hydroxy-4-phenyl-2-cyclopenten-1-one (24). To a suspension of 0.08 g (2 mmol) of NaH (60% dispersion) in 5 mL of THF was added dropwise a solution of 0.23 g (2 mmol) of methyl acetoacetate in 3 mL of THF with stirring and ice cooling. After 30 min, a solution of 0.56 g (2 mmol) of **11** in 5 mL of THF was added to the mixture. The mixture was stirred for 2 h with ice–salt cooling and then for an additional 3 h with ice cooling. The reaction mixture was condensed under reduced pressure below 30 °C. The resulting residue was acidified with 10% HCl under ice cooling. The crystals separated were recrystallized from ethanol to give 0.52 g (92%) of **24** as colorless needles: mp 191–192 °C; IR (KBr) 2880, 1680 (C=O), 1605 (C=O, C=C), 1210 (P=O), 1060, 1025 (POC) cm^{-1}; NMR (CF_3CO_2H) δ 3.28–4.08 (m, 2 H, 5-CH_2), 3.87 (d, 3 H, J = 10.5 Hz, $POCH_3$), 3.98 (d, 3 H, J = 10.5 Hz, $POCH_3$), 6.03 (s, 1 H, 2-H), 7.30–7.72 (m, 5 H, aromatic protons). Anal. Calcd for $C_{13}H_{15}O_5P$: C, 55.33; H, 5.32. Found: C, 55.35; H, 5.27.

4-(Dimethylphosphono)-3-hydroxy-4-(*p*-methoxyphenyl)-2-cyclopenten-1-one (25). Following the procedure described above, reaction of 0.62 g (2 mmol) of **12a** with 0.23 g (2 mmol) of methyl acetoacetate in the presence of 0.08 g (2 mmol) of NaH (60% dispersion) gave 0.49 g (79%) of **25** as colorless needles (from ethyl acetate): mp 186–187 °C; IR (KBr) 1680 (C=O), 1605 (C=O, C=C), 1240 (P=O), 1070, 1035 (POC) cm^{-1}; NMR (CF_3CO_2H) δ 3.13–3.96 (m, 2 H, 5-CH_2), 3.73 (d, 3 H, J = 10.8 Hz, $POCH_3$), 3.85 (d, 3 H, J = 10.8 Hz, $POCH_3$), 3.92 (s, 3 H, OCH_3), 5.92 (s, 1 H, 2-H), 6.98–7.67 (m, 4 H, aromatic protons). Anal. Calcd for $C_{14}H_{17}O_6P$: C, 53.85; H, 5.45. Found: C, 54.02; H, 5.62.

Methylation of the Pentenone 24. Method 1. A solution of 0.28 g (1 mmol) of the pentenone **24**, 10 mg of *p*-toluenesulfonic acid, and 1 mL of absolute methanol in 10 mL of dry benzene was heated under reflux for 6 h. Evaporation of the solvent gave an oily residue, which was dissolved in 10 mL of ethyl acetate. The solution was washed with 5 mL of 10% NaOH and then with water. Evaporation of ethyl acetate gave a crystalline substance, which was recrystallized from benzene–hexane to afford 0.23 g (78%) of 5-(dimethylphosphono)-3-methoxy-5-phenyl-2-cyclopenten-1-one (**26**) as colorless prisms: mp 91–92 °C; IR ($CHCl_3$) 1695 (C=O), 1610 (C=C), 1275 (P=O), 1065, 1040 (POC) cm^{-1}; NMR ($CDCl_3$) δ 2.95–3.83 (m, 2 H, 4-CH_2), 3.48 (d, 3 H, J = 10.5 Hz, $POCH_3$), 3.73 (d, 3 H, J = 10.5 Hz, $POCH_3$), 3.83 (s, 3 H, OCH_3), 5.97 (t, 1 H, 2-H), 7.20–7.76 (m, 5 H, aromatic protons). Anal. Calcd for $C_{14}H_{17}O_5P$: C, 56.76; H, 5.74. Found: C, 57.01; H, 5.64.

Method 2. A solution of 0.24 g (0.9 mmol) of the pentenone **24** in 2 mL of ethanol was added to a solution of excess diazo-

(10) The 1-(dimethylphosphono)-5-oxo-4-oxaspiro[2.3]hexane used for the reaction is a mixture of *E* and *Z* isomers.

methane in 20 mL of ether. The mixture was allowed to stand overnight at room temperature. The reaction mixture was evaporated to give an oily residue, which was subjected to column chromatography on silica gel (15 g). The column was developed with 0.3 L of chloroform–hexane (1:3) and successively with 0.3 L of chloroform–hexane (1:1).

Elution with chloroform gave 98 mg (38%) of **26**. Subsequent elution with ethyl acetate gave an oily substance, which was allowed to stand overnight at −20 °C to give a crystalline substance. Purification by recrystallization from ether–petroleum ether gave 91 mg (35%) of 4-(dimethylphosphono)-3-methoxy-4-phenyl-2-cyclopenten-1-one (**27**) as colorless needles: mp 78–80 °C; IR ($CHCl_3$) 1690 (C=O), 1605 (C=C), 1255 (P=O), 1070, 1040 (POC) cm^{-1}; NMR ($CDCl_3$) δ 2.58–3.70 (m, 2 H, 5-CH_2), 3.57 (d, 3 H, J = 10.6 Hz, $POCH_3$), 3.70 (d, 3 H, J = 10.6 Hz, $POCH_3$), 3.97 (s, 3 H, OCH_3), 5.56 (d, 1 H, J = 2.0 Hz, 2-H), 7.26–7.80 (m, 5 H, aromatic protons). Anal. Calcd for $C_{14}H_{17}O_5P$: C, 56.76; H, 5.74. Found: C, 56.69; H, 5.86.

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Registry No. **4**, 28447-24-7; **5**, 26584-15-6; **6**, 16965-72-3; **7**, 41920-22-3; **8**, 39980-21-7; **9a**, 73558-63-1; **9b**, 73558-64-2; **10a**, 73558-65-3; **10b**, 73558-66-4; **11a**, 73558-67-5; **11b**, 73558-68-6; **12a**, 73558-69-7; **12b**, 73558-70-0; **13a**, 73558-71-1; **13b**, 73558-72-2; **14**, 5353-66-2; **15a**, 73558-73-3; **15b**, 73558-74-4; **16**, 73558-75-5; **17**, 73558-76-6; **18a**, 73558-77-7; **18b**, 73558-78-8; **18c**, 73558-79-9; **18d**, 73558-81-3; **19a**, 73558-81-3; **19b**, 73558-82-4; **19c**, 73558-83-5; **19d**, 73558-84-6; **20**, 73558-85-7; **21**, 73558-86-8; **22a**, 73558-87-9; **22b**, 73558-88-0; **23a**, 73558-89-1; **23b**, 73558-90-4; **24**, 73558-91-5; **25**, 73558-92-6; **26**, 73558-93-7; **27**, 73558-94-8; diketene, 674-82-8; *O*-phenylenediamine, 95-54-5; methyl acetoacetate, 105-45-3; *p*-toluidine, 106-49-0; *p*-anisidine, 104-94-9; *p*-nitroaniline, 100-01-6; *p*-chloroaniline, 106-47-8; resorcinol, 108-46-3; phloroglucinol, 108-73-6.

Supplementary Material Available: Listings of IR and ^1H NMR data for all new compounds in Tables II–IV: Table V, **9a,b–13a,b**; Table VI, **18a–d** and **19a–d**; Table VII, **22a,b** and **23a,b** (5 pages). Ordering information is given on any current masthead page.

Reactivity of 1,3-Diimines. Reaction with Heterocumulenes

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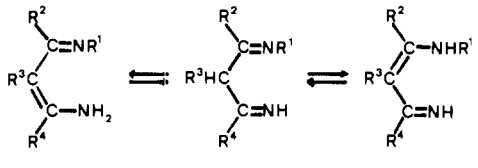
1,3-Diimines **1** react with isocyanates and isothiocyanates **2** to give, as the major products, different 2-oxo- and 2-thiopyrimidines **9** and **10**. The formation of these products can be explained by two different reaction paths that involve an addition reaction followed by an electrocyclic ring closure. The nature of the group R^1 in **1** plays a basic role in the result of the process. Open-chain intermediate products **3** have been isolated and characterized for the first time in a cyclization reaction with diimines **1**.

Diimines **1** are readily prepared by reaction of Schiff bases with saturated nitriles in the presence of aluminum trichloride as the catalyst.[1] These diimines can be isolated in their tautomeric forms **1a** and (or) **1b**.

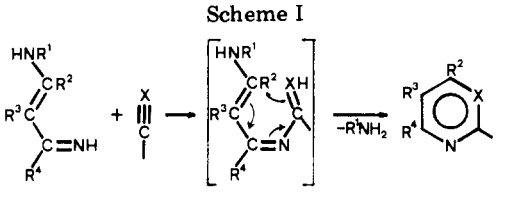


1a ≈ **1** ≈ **1b**

An examination of their structure shows that both tautomers can be considered to be 1-azabutadiene derivatives, and, hence, they might be suitable substrates to undergo Diels–Alder cycloadditions. This possibility is highly problematic according to results reported in the references, since 1-azabutadiene derivatives show, in general, little aptitude to give this type of cycloaddition.[2]

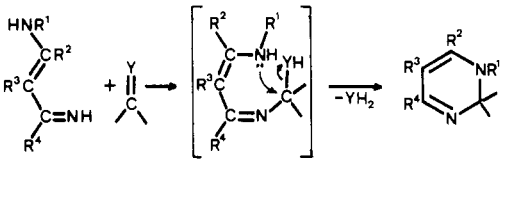
Our own experiments on the reactivity of **1** fully support those results previously reported for 1-azabutadiene derivatives; the reaction of **1** with excellent dienophiles, such as tetracyanoethylene[3] or azodicarboxylic acid ester,[4] affords products whose structure does not correlate with that of cycloaddition adducts.

Scheme I



X = N, C-CO_2Et

Scheme II



Y = NR, O, $(OEt)_2$

However, diimines **1** react with saturated nitriles and acetylenedicarboxylic acid ester to give rise to convenient synthetic methods for the preparation of pyrimidines[5] and pyridines,[6] respectively. Although these compounds could

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